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Influence of SiO_2 buffer layer on the crystalline quality and photoluminescence of ZnO thin films

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Abstract. In this work, a SiO_2 buffer layer was first grown on Si substrate by thermal oxidation, and then ZnO thin films were deposited on SiO_2 buffer layer and Si substrate by electron beam evaporation and sol-gel method. The influence of SiO_2 buffer layer on the crystalline quality and photoluminescence of the films was investigated. The analyses of X-ray diffraction (XRD) showed that all the ZnO thin films had a hexagonal wurtzite structure and were preferentially oriented along the c-axis perpendicular to the substrate surface. The SiO_2 buffer layer improved the crystalline quality and decreased the stress in ZnO thin films. The surface morphology analyses of the samples indicated that ZnO thin films deposited on SiO_2 buffer layers had densely packed grains which obviously increased compared with those grown on bare Si substrate. The photoluminescence spectra of the samples showed that the ZnO thin films deposited on SiO_2 buffer layers had stronger ultraviolet emission performance. The results suggest that SiO_2 buffer layer can improve the crystalline quality and ultraviolet emission of ZnO thin films.

1. Introduction

ZnO is an important compound semiconductor with excellent chemical and thermal stability. It has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. Lots of research results show that ZnO thin films and nanostructures have high excitonic emission efficiency. So far, ZnO materials are still studied mainly in the form of thin films. ZnO thin films can be used to fabricate many optoelectronic devices such as ultraviolet light-emitting diodes [1], ultraviolet lasers [2], nonvolatile memories [3], optical waveguides [4], ultraviolet photoconductive detectors [5], etc. Many research results indicate that the optical and electrical properties of ZnO thin films are directly connected with their crystallization quality. Therefore, if one wants to fabricate ZnO-based devices with good optoelectronic performance, he has to prepare high-quality ZnO thin films first. It is well-known that the crystalline quality of ZnO thin films has a close connection with the substrates. Many materials have been used as ZnO film substrates such as sapphire, MgO, GaN, Si, quartz, glass, etc. Compared with other materials, Si has some advantages like plentiful raw materials and mature

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growth technique of single crystal. Especially, Si material is the cornerstone of the current semiconductor microelectronics industry. If high-quality ZnO thin films can be grown on Si substrate, it will be beneficial for effective integration of optoelectronic devices with Si IC technology. However, the mismatch of lattice constants and thermal expansion coefficients between ZnO and Si are large. What is more, when ZnO thin films are directly deposited on bare Si substrate or these films are annealed at high temperatures, Si atoms on the substrate surface are easy to "capture" oxygen atoms from ZnO thin films [6, 7], which will result in many oxygen vacancies in the films. The above-mentioned factors all lead to the decline of crystalline quality of ZnO thin films. Therefore, many researchers use buffer layers between ZnO thin films and Si substrates in order to improve the crystalline quality of the films. Some groups used ZnO homogenous buffer layer [8], others applied heterogeneous buffer layers such as GaN [9], Y_2O_3 [10], AlN [11], Ti [12], etc.

So far, ZnO thin films have been prepared by many techniques such as pulsed laser deposition, electron beam evaporation, magnetron sputtering, chemical vapor deposition, molecular beam epitaxy, sol-gel method, etc. Among these techniques, sol-gel method has attracted much attention due to many advantages like low cost, simple deposition procedures, no need of vacuum deposition conditions, easier fabrication of large-area film, easier control of composition, being able to deposit thin films on complex-shaped substrates, etc. Moreover, electron beam evaporation is also an important technique for fabrication of ZnO thin films. In this work, ZnO thin films were deposited on SiO_2 buffer layer and Si substrate by E-beam evaporation and sol-gel method. We studied the influence of SiO_2 buffer layer on the crystalline quality and photoluminescence of ZnO thin films and compared the difference of ZnO/ SiO_2 films prepared by the two techniques.

2. Experimental

2.1. Cleaning of Si substrate and formation of SiO_2 buffer layer

One-side polished Si (100) chips were used as film substrates. Si chips were first rinsed in acetone and ethanol, respectively, with ultrasonic vibration for 10 min. Then the Si chips were put into diluted HF solution for 3 min to remove native SiO_2 layer and subsequently rinsed in deionized water. At last, the Si chips were naturally dried in a clean glass chamber. An amorphous SiO_2 buffer layer of ~50 nm thickness was formed on the Si chip surface by thermal oxidation.

2.2. Deposition of ZnO thin films by electron beam evaporation

ZnO thin films were deposited on a bare Si substrate and a SiO_2 buffer layer, respectively, by electron beam evaporation (PMC90S, Protech Korea Ltd.). High purity (99.999%) ZnO particles were used as source material. When ZnO thin films were deposited, the Si substrates were placed on a sample holder which was about 1.5 m from evaporation source and rotated at 40 rpm. The substrate temperature was 200 ℃; the working pressure (Ar+O_2) was 2.3×10^{-2} Pa. A quartz crystal controller (IC5) was used to control the thickness of the films. The deposited film thicknesses were 150 nm. The film deposited on a bare Si substrate was labelled as sample A; the other one deposited on a SiO_2 buffer layer was labelled as sample B. The two samples were annealed in air at 600℃ for an hour.

2.3. Deposition of ZnO thin film by sol-gel method

Zinc acetate, ethanol and monoethanolamine were used to prepare ZnO sol. In this solution, the concentration of zinc acetate was 0.40 mol/L. After the ZnO sol was aged for 24 h at room temperature, ZnO thin films were deposited on SiO_2 buffer layer by spin-coating method. The spin-coating time was 30 s. In the beginning 10 s, the spin-speed was 1500 rpm; in the latter 20 s, the spin-speed was 2500 rpm. After each spin-coating, the sample was put into a furnace kept at 350℃ to be dried and given a pre-heating treatment for 10 min. The procedure from spin-coating to pre-heating treatment was repeated several times in order to increase the film thickness to ~150 nm. This sample was annealed in air at 600℃ for an hour and labelled as sample C.

2.4. Characterization of structure and luminescence property of ZnO thin films

The crystal phase and crystalline orientation of the samples were investigated by an X-ray diffractometer (Bruker D8 Advance). The surface morphology was analyzed by an atomic force microscope (CSPM4000) in contact mode. The photoluminescence spectra were used to analyze the luminescence behavior of the samples. The excitation source was a Xe lamp and the excitation wavelength was 325 nm. All the measurements were performed at room temperature in air.

3. Results and discussion

3.1. Influence of SiO_2 on the structures of ZnO thin films

Fig.1 shows the XRD patterns of the three samples. It can be seen from Fig.1 that all the samples have a diffraction peak at 34.5° or so, which corresponds to the diffraction of (002) plane of wurtzite-structured ZnO. This indicates that all the ZnO thin films have a hexagonal wurtzite structure and are preferentially oriented along the c-axis perpendicular to the substrate surface. For sample A, B and C, the (002) peak lies at 34.65°, 34.50° and 34.45°, respectively. The position of the (002) peak is associated with the stress in the ZnO thin films. As for the stress-free ZnO powder, its (002) peak lies at 34.43°. From the above data, it is obvious that the (002) peak position of ZnO thin films grown on SiO_2 buffer layer is closer to that of stress-free ZnO powder. This suggests that the usage of SiO_2 buffer layer decreases the stress in the film. For the stress in the ZnO thin film deposited on the bare Si substrate, it mainly results form the mismatch of lattice constants and thermal expansion coefficients between ZnO and Si substrate. Fig.2 shows the crystallite size and film stress derived from XRD data. The crystallite size is calculated by Scherrer formula and film stress is calculated according to the formula in the Ref. [13]. It can be seen from Fig.2 that due to the decrease of the film stress, the crystallites further grow up. The above results suggest that SiO_2 buffer layer improves the crystalline quality of ZnO thin films.

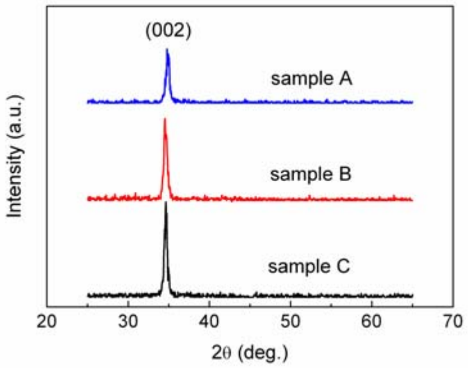

Figure 1. XRD patterns of the ZnO thin films.

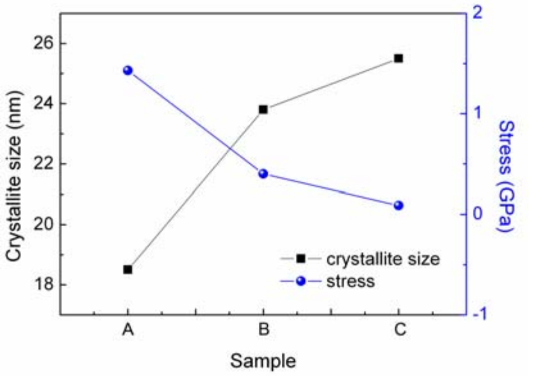

Figure 2. The crystallite sizes and stress of the ZnO thin films.

Fig.3 displays the surface morphology images of the samples. The scanning area is $4\mu m \times 4\mu m$. From Fig.3, it is obvious that all the samples have uniform grains and dense structure. Compared with sample A, the grains of sample B and C apparently increased. This is in agreement with the results derived from XRD data. However, the grains observed by AFM are bigger than that derived from XRD data. It is likely that a grain consists of several crystallites. The similar results have been also observed in many studies [14, 15].

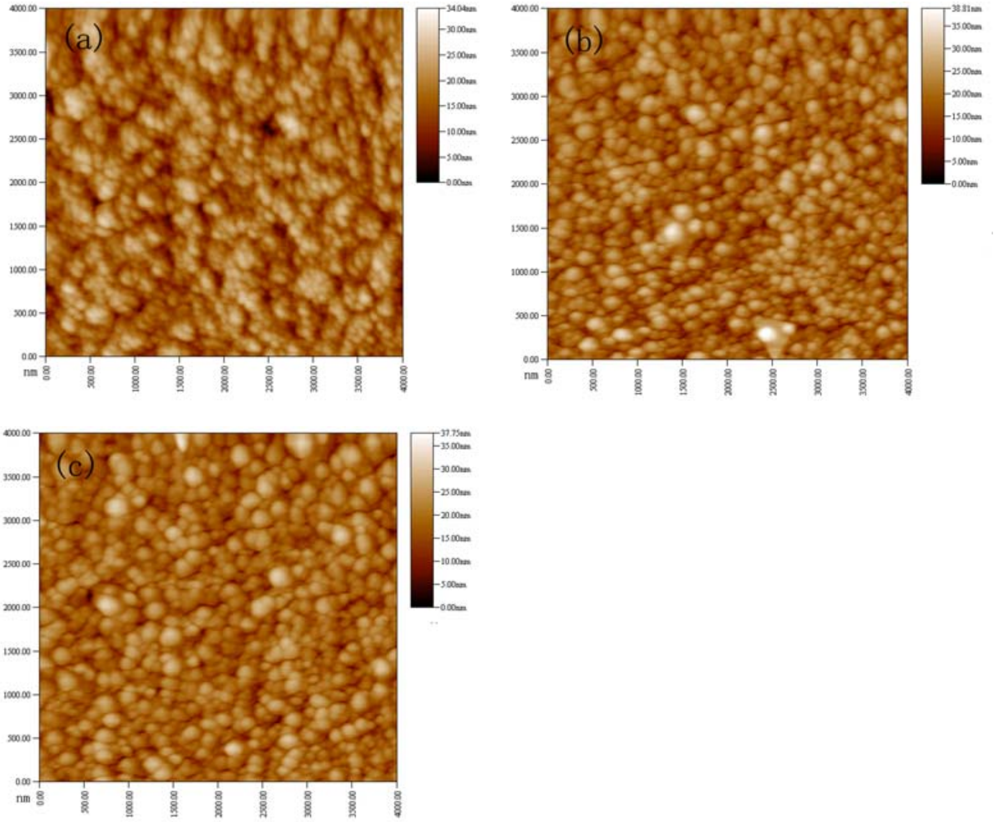

Figure 3. Surface morphology images of sample A (a), B (b), and C (c).

3.2. *Influence of SiO_2 buffer layer on the photoluminescence of ZnO thin films*

Fig.4 shows the photoluminescence spectra of the samples. As for sample A, besides an ultraviolet emission peak centered at 382 nm or so, it has a weak and wide green emission band. Compared with sample A, sample B and C have a stronger ultraviolet emission peak and weaker visible emissions; the full width at half maximum of the ultraviolet emission peaks is decreased.

In regard to the ultraviolet emission centered at 382 nm, it is generally accepted that it results from the recombination of free excitons [16, 17]. It is well-known that the density of free excitons is closely connected with the crystalline quality of ZnO thin films. Only the films with high crystalline quality and low defect density could have high density of free excitons. From the photoluminescence spectra, it can be seen that ZnO thin films deposited on SiO_2 buffer layers have stronger ultraviolet emission and lower visible emissions, which means that SiO_2 buffer layer improved the crystalline quality of ZnO thin films and reduced the density of native defects. Although both sample B and C are deposited on SiO_2 buffer layer, the ultraviolet emission of sample C seems stronger than that of sample B. Previously, Taschuk et al. [18] reported that the ultraviolet emission efficiency of the ZnO thin film deposited by sol-gel method was higher than those of ZnO thin films deposited by electron beam evaporation, pulsed laser deposition and magnetron sputtering. It is probably connected with the unintentionally doped hydrogen in the sample C deposited by the sol-gel process [19]. As for the green emission of ZnO thin films, it is often observed in the photoluminescence spectra. However, the green emission mechanism is unclear up to now. Some researchers ascribe the green emission to oxygen vacancy defects in ZnO [20, 21], others speculate that the green emission probably results from Zn vacancy defects [22] or antisite oxygen [23, 24]. We tend to think the green emission originates from oxygen vacancy defects. For the ZnO thin film deposited on the bare Si substrate by electron beam evaporation, the oxygen vacancies in the film is mainly connected with the two following factors: (1) the film growth environment is oxygen-deficient, which easily leads to oxygen vacancies in ZnO thin films; (2) the Si atoms on the substrate surface easily “capture” oxygen atoms from ZnO thin films. After the SiO_2 buffer layer is used, it effectively prevents Si atoms to “capture” oxygen from ZnO thin films, decreasing the density of oxygen vacancy. Accordingly, the green emission is reduced. For sample B, its growth environment is oxygen-deficient, so there are still some oxygen vacancies in the films. However, the sol-gel process offers the film an oxygen-surplus growth environment. As a result, sample C has almost no green emission related to oxygen vacancy defects.

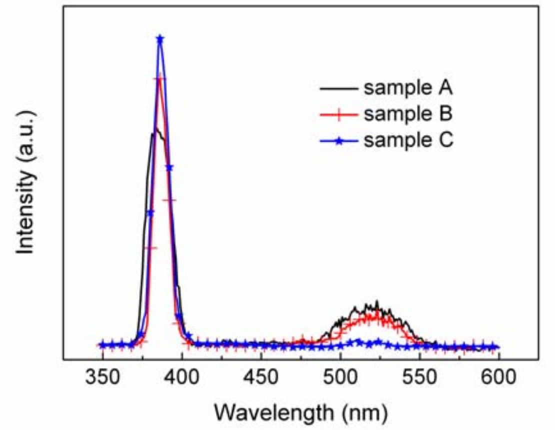

Figure 4. Room-temperature photoluminescence spectra of the ZnO thin films.

4. Conclusions

In this work, ZnO thin films were deposited on a SiO_2 buffer layer and a bare Si substrate by E-beam evaporation and sol-gel method. The influence of SiO_2 buffer layer on the structures and photoluminescence of the samples were studied. All the samples were wurtzite-structured and ZnO grains grew preferentially along the c-axis perpendicular to the substrate surface. ZnO thin films deposited on SiO_2 buffer layer had better crystalline quality. Photoluminescence spectra showed that the ultraviolet emission of sample B and C was increased and visible emission was reduced. The above results suggest that SiO_2 buffer layer can improve the crystalline quality and enhance the excitonic emission of ZnO thin films. The growth of SiO_2 buffer layer by thermal oxidation and ZnO thin films by sol-gel method is simple and low-cost, but the prepared film has good crystallization and excitonic emission. Therefore, it is a good method to combine sol-gel method with thermal oxidation to prepare high-quality ZnO thin films on Si substrates.

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